A Study on Electron Irradiation Effects in Hydrated Cobalt Ferricyanide Using Mössbauer Spectroscopy (Commemoration Issue Dedicated to Professor Sakae Shimizu on the Occasion of his Retirement)

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Communicaton

A Study on Electron Irradiation Effects in Hydrated Cobalt Ferricyanide Using Mössbauer Spectroscopy

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Recent works[1-4] on irradiation experiments with complexes have reported that low-spin Fe^{III} is reduced to Fe^{II} after the irradiation. The same effect has been obtained by heating the sample. In this report we give Mössbauer spectroscopic measurements with hydrated cobalt ferricyanide irradiated by electron beams.

The complex was prepared by mixing slowly 0.01 N cobalt chloride and potassium ferricyanide. The precipitation was filtered, washed by ethanol and dried. The complex powder of about 250 mg was packed in an aluminum ring of 20 mm diameter covered with aluminum foil. The samples were irradiated at liquid nitrogen temperature with 1 MeV electron beams of 90 μA for 10 minutes and 77 μA for 1 hour. The Mössbauer measurements were performed at liquid nitrogen temperature, a) just after the irradiation, b) after annealing the irradiated samples at room temperature for 50 days, and c) after exposing the annealed powder to fresh air for 1 hour.

Figures 1 and 2 show the observed spectra which are resolved into several Lorentzian peaks of low-spin Fe^{III} and Fe^{II} and high-spin Fe^{3+} by least-square fitting. The Mössbauer parameters obtained are listed in Table I. We can see the following results from Table I. The reduction to low-spin Fe^{II} is the main effect of the irradiation. However, a part of the remaining Fe^{III} species changes to high-spin Fe^{3+} by the annealing. The reason would be supposed that cyanide linkages connected to low-spin iron species become unstable by the irradiation and the cyanide complex ions are decomposed by the annealing. When the sample is irradiated with very high dose, Fe^{3+} ions come from, as well as all of Fe^{III}, a part of Fe^{II} species formed by the irradiation. This dose dependence of the annealing effect implies that, probably due to H′ radicals formed by radiolytic decomposition of the water ligands[2], low-spin Fe^{III} is reduced to Fe^{II} at the first stage of the irradiation and the cyanide linkages become unstable with further irradiation. The instability of Fe^{II} only at the very high dose irradiation shows that the

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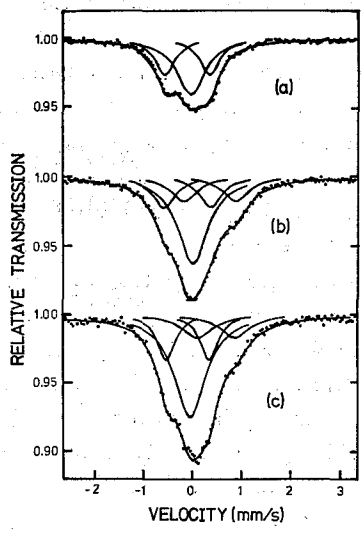

Fig. 1. Mössbauer spectra of cobalt ferricyanide irradiated with 90 μA of 1 MeV electrons for 10 minutes. a) Irradiated. b) Annealed for 50 days after irradiation. c) Exposed to fresh air after irradiation and annealing.

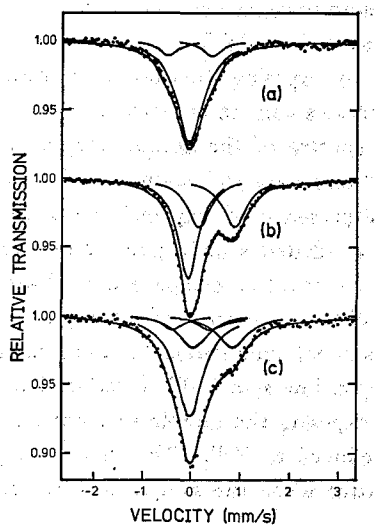

Fig. 2. Mössbauer spectra of cobalt ferricyanide irradiated with 77 μA of 1 MeV electrons for 1 hour. a) Irradiated. b) Annealed for 50 days after irradiation. c) Exposed to fresh air after irradiation and annealing.

Table I. Mössbauer Parameters of the Irradiated Complex

Species		IS (mm/sec)	QS (mm/sec)	Width (mm/sec)	Intensity (%)
			90 μA-10 min.		
a	Fe^{III}	−0.10	0.92	0.48	47.4
	Fe^{II}	−0.03	——	0.70	52.6
b	Fe^{III}	−0.09	0.95	0.53	25.8
	Fe^{3+}	0.37	1.06	0.61	24.1
	Fe^{II}	0.01	——	0.74	50.1
c	Fe^{III}	−0.09	0.88	0.43	25.9
	Fe^{3+}	0.49	0.77	0.73	22.0
	Fe^{II}	−0.04	——	0.80	52.1
			77 μA-1 hour		
a	Fe^{III}	−0.03	0.90	0.44	16.9
	Fe^{II}	−0.03	——	0.66	83.1
b	Fe^{3+}	0.50	0.72	0.60	52.9
	Fe^{II}	−0.08	——	0.51	47.1
c	Fe^{III}	−0.02	0.76	0.55	12.1
	Fe^{3+}	0.44	0.81	0.70	34.9
	Fe^{II}	−0.03	——	0.68	52.9

(a) Irradiated.
(b) Annealed for 50 days after irradiation.
(c) Exposed to fresh air after irradiation and annealing.

cyanide linkages connected to Fe^{II} are more stable against the irradiation than those connected to Fe^{III}.

By exposing the sample to fresh air, no conspicuous changes of the relative peak intensities can be recognized when the irradiation dose is not very high. However, as to the spectra of the sample irradiated with very high dose, approximately one third of Fe^{3+} ions vary to low-spin atoms. The above fact means that the presence of air, probably presence of oxygen, causes to coordinating of CN groups around iron atoms in the irradiated sample powder in which too much Fe^{3+} ions exist.

In order to compare the effects by irradiation with those by heating the complex, we observed spectra of a sample heated at 200°C for 1 hour as shown in Fig. 3. The Mössbauer parameters for the heated complex are shown in Table II. By heating the sample, low-spin Fe^{III} is reduced to Fe^{II}. The relative intensity of Fe^{3+} is rather small. By exposing the sample to fresh air for 1 hour, approximately half of the remainig Fe^{III} is reduced to Fe^{II}. This reduction process did not happen in the irradiated complex powder when the sample was exposed to fresh air, as mentioned above.

Table II. Mössbauer Parameters of the Heated Complex

	Species	IS (mm/sec)	QS (mm/sec)	Width (mm/sec)	Intensity (%)
a	Fe^{III}	−0.03	1.35	0.90	61.6
	Fe^{3+}	0.57	0.80	0.64	9.2
	Fe^{II}	−0.08	—	0.86	29.2
b	Fe^{III}	0.05	1.10	0.85	28.4
	Fe^{3+}	0.56	0.75	0.59	11.1
	Fe^{II}	−0.01	—	0.68	60.5

(a) Heated. (b) Exposed to fresh air after heating

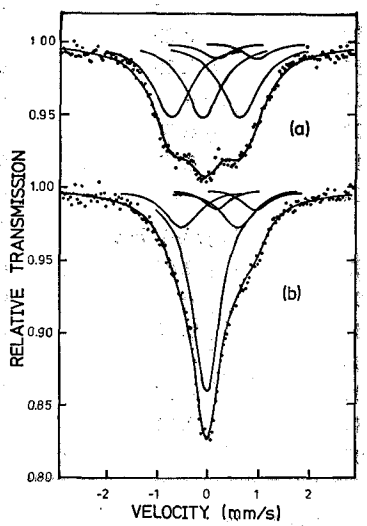

Fig. 3. Mössbauer spectra of cobalt ferricyanide heated at 200°C for 1 hour. a) Heated. b) Exposed to fresh air after heating.

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